

Potential Health and Environmental Effects of Trace Elements and Radionuclides from Increased Coal Utilization

by R. I. Van Hook*

This report addresses the effects of coal-derived trace and radioactive elements. A summary of our current understanding of health and environmental effects of trace and radioactive elements released during coal mining, cleaning, combustion, and ash disposal is presented. Physical and biological transport phenomena which are important in determining organism exposure are also discussed. Biological concentration and transformation as well as synergistic and antagonistic actions among trace contaminants are discussed in terms of their importance in mobility, persistence, availability, and ultimate toxicity. The consequences of implementing the President's National Energy Plan are considered in terms of the impact of the NEP in 1985 and 2000 on the potential effects of trace and radioactive elements from the coal fuel cycle. Areas of needed research are identified in specific recommendations.

Introduction

Combustion of coal for the production of electrical and thermal energy is not without attendant health and environmental effects. Numerous reports have been prepared in recent years concerning these effects relative to our current pattern of coal utilization of approximately 650 million tons per year. Most studies have dealt with specific parameters of coal utilization such as health effects of coal combustion (1), toxicity of coal-derived trace elements (2), effects of coal-derived trace elements on water quality (3), and effects of coal-derived radionuclides (4). Recently several reports have appeared addressing an integrated assessment of coal utilization (5-8) and these reports have been utilized extensively in developing the following materials. Specifically, ERDA 77-64 "Effects of Trace Contaminants From Coal Combustion" (5) has been used as a basis for the present analysis and sections of that report have been repeated verbatim with new information inserted in appropriate locations.

The President's National Energy Plan (NEP) contains assumptions which bear directly on questions about health and environmental impacts of trace elements and radionuclides from increased coal utilization. The most important assumptions are that annual coal production will grow from 650 million tons (15.3 quads) in 1975 through 1,200 million tons (28.2 quads) in 1985 to 1,910 million tons (44.9 quads) in 2000, and that by 1985, all emission sources will be in full compliance with environmental regulations promulgated by the U.S. Environmental Protection Agency (EPA) and by individual states. The NEP is based on application of the Best Available Control Technology (BACT) being applied to all new or expanded utility and industrial boilers. As outlined in Public Law 95-95, the 1977 amendments to the Clean Air Act of 1970, BACT is to replace the New Source Performance Standards (NSPS). Although not directly addressed in the NEP, fly ash and scrubber sludge may be defined as hazardous substances under the Resource Conservation and Recovery Act of 1976. This will have a significant impact on allowable release rates from landfills and settling ponds used in fly ash disposal. The Surface Mining and Reclamation Act of 1977 will play a major

*Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

role in determining coal availability by placing more stringent regulations on levels of mine drainage and on reclamation practices for both existing and new mines. The NEP assumes no advanced coal combustion or coal liquefaction before 2000. Coal gasification is assumed to contribute 1.2 quads by 1985 and 3.8 quads by 2000 with attendant solid waste and water use problems.

The objective of the present paper is to discuss the current status of our understanding of health and environmental effects of trace elements and radionuclides from coal utilization and to estimate the probable impacts of increasing coal utilization as envisioned in the NEP. A discussion of environmental and biological transport is included because transport and transformations of hazardous elements determine organism exposure and ultimate toxicity. It should be pointed out early that accurate, inexpensive analytical techniques for determining amounts and chemical forms of trace contaminants are essential to understanding and evaluating transport and effects of these materials. With the exception of transportation, which is covered elsewhere, the complete coal fuel cycle is addressed in this study.

Summary

Trace elements and radionuclides potentially hazardous to human health and ecosystems are present in coal. Trace elements of concern include, among others, As, Be, Cd, Cr, F, Hg, Ni, and Pb. Concentrations of these elements vary considerably among coal types. Radioactive elements of concern in coal include ^{235}U , ^{238}U , ^{232}Th , and associated daughter products. Concentrations of radionuclides in coal are generally less variable than those of trace elements, values of 1 ppm for U and 2 ppm for Th being reasonable national averages.

Trace and radioactive elements can enter the environment prior to coal combustion through runoff from mining, cleaning, and storage operations; during combustion in atmospheric emissions of respirable particulates and volatile elements; and following combustion through runoff and leachate infiltration into ground water from bottom ash, fly ash, and scrubber sludge deposited in settling ponds and landfills. Trace contaminants released to the environment from the coal fuel cycle may result in exposure of organisms at considerable distances due to atmospheric transport of particulate and gaseous forms, or contaminants from solid wastes (ash) may reach drinking water supplies through hydrologic transport in ground and surface waters.

At nearly every point along physical transport

pathways in aquatic and terrestrial environments, opportunities exist for interactions of trace elements with life forms. Organisms, especially microorganisms in aquatic environments, can absorb, concentrate, and transform trace and radioactive elements into more concentrated forms or more toxic compounds. Biotransformation of trace and radioactive elements is particularly important in determining effects on man and other organisms, since it is the molecular form of these contaminants that determines their persistence, availability, bioaccumulation, and toxicity. Bioaccumulation is of particular concern for elements such as Cd, Hg, and Pb because current intake levels for these substances are near tolerable human health limits.

Ecological effects of trace and radioactive elements from the coal fuel cycle are presently or will be associated primarily with mining, cleaning, and solid waste (ash, sludge) disposal. The acidic nature of mine drainage from eastern coal fields tends to hold metal ions in solution and promotes their transport to surface and ground waters. Acid mine drainage from inactive mines in the eastern United States is the greatest single source of drainage and transport to aquatic environments, and is very difficult to control. Western coal generally lacks acid-forming substances, although increased salinity of surface and ground waters in western coal regions could become a problem due to soluble salts in mine spoils. During overburden removal for strip mining, ground water aquifers are commonly intercepted; hazardous elements may enter these disturbed aquifers. Impacts associated with elements in runoff and leachate from coal cleaning and storage are similar to but of lesser magnitude than those associated with coal mining.

Concentrations of trace contaminants in atmospheric emissions from coal-fired power plants do not appear to be a significant ecological hazard. Trace element concentrations in soils fall rapidly with distance from power plants and tend to be at background levels at distances ≥ 3 km from the plant. With installation of efficient electrostatic precipitators, atmospheric emissions of trace elements should not be acutely harmful to vegetation and other biota, especially beyond a 3 km radius. Only fluorine appears to deserve special watching. Likewise, the potential for chronic toxicity to ecosystems is relatively low, except in local areas already enriched with a particular element. However, sublethal, chronic or synergistic effects of trace elements on ecosystems have received little attention.

About 92% of particulate materials produced in utility boilers is removed by electrostatic precipitators. Fly ash, bottom ash and scrubber sludge

all contain trace and radioactive elements. These are generally released to ground water at low concentrations, with attenuation occurring very close to the disposal site. Very little information is available on the chemical form, bioavailability and toxicity of these contaminants. By 1985, 60 to 100 million tons of fly ash with elevated levels of trace elements will be annually discharged into settling basins or landfills situated in close proximity to coal-fired power plants. Elements such as As, Cd, Co, Hg, Ni, Pb, Se, U, and Zn all exhibit mobilization rates from these deposits that are larger than 10% of the natural weathering rates. Cadmium, Hg, and U appear to be mobilized through coal combustion at rates comparable to their natural weathering rates. These elements have a definite potential for runoff to surface waters and leachate intrusion into ground water and their concentrations should be monitored closely.

There is reasonable concurrence that some trace contaminants in coal may constitute human health problems from either direct toxicity or risk of cancer. Among those most toxic to man are Cd, Hg, and Pb, intake levels of which are already near tolerable health limits. Three elements — As (III), Cr (VI), and Ni (carbonyl) — are accepted as having high carcinogenic importance to man. Of these, As (III) and Cr (VI) probably occur in fly ash leachate, but at unknown concentrations, while Ni (carbonyl) does not occur. There is little or no teratogenic potential from Cd, Hg, or Se compounds at concentrations found in atmospheric emissions or fly ash leachate. The potential for contamination of drinking water supplies by trace elements in leachates from settling ponds or landfills is very real and needs to be evaluated. As previously noted, ash disposal sites will increase in both size and number, amounting to 60 to 100 million tons of wastes annually by 1985.

Estimated annual release rates for radionuclides from a 1000 MW(e) coal-fired power plant amount to 0.04 to 0.35 mrem/yr whole body dose, as a maximal annual dose commitment per individual. To compare the magnitude of radiation from coal combustion emissions, it is useful to use dose equivalent rates for natural background and coal emissions. The dose equivalent rate for the whole body from all natural radiation sources is 80 ± 40 mrem/yr. The corresponding coal combustion radiation rate is 0.007 mrem/yr. On this basis, atmospheric releases of radionuclides from increased coal combustion do not represent a significant public health problem unless coal containing > 5 ppm U come into general use. Radionuclide releases from ash disposal sites have not been evaluated, and depending upon ash leaching rates, could become a significant human health consideration.

There are several areas of uncertainty which should be pointed out. These areas are listed below; recommendations for needed research are listed at the conclusion of this report.

(1) The chemical form of trace elements is very important as a determinant of transport through the environment and of toxic effects on health and ecosystems. Most studies of coal emissions and leachates focus on simple elemental analysis. Lack of knowledge of chemical species of trace elements precludes making a confident and adequate assessment of the potential health and ecological effects of trace elements from coal utilization.

(2) Potential contamination of drinking water supplies by several toxic or radioactive elements in leachates from waste disposal presents a real public health problem. The chemical form of each element may be significantly altered by microorganisms in the physical transport process, and these chemical forms will determine the rate of environmental transport, the bioaccumulation and toxicity of these elements. Too little is known about these processes.

(3) Given that several trace elements in leachates exhibit mobilization rates that are larger than 10% of natural weathering rates, do these elements effectively remain in settling basins or are they injected into waterways and into food chains? Unquestionably, the movement of trace elements from coal combustion disposal sites should be regarded as a potentially significant health problem and bears intensive monitoring in some sites.

(4) While the ambient atmospheric loading of trace elements does not appear to be as great a potential problem as intrusion into waterways from leachates, there is a need to monitor atmospheric concentrations at selected sites. Few data exist on trace element ambient concentrations, fallout and re-entrainment from disposal sites. Atmospheric and environmental levels of cadmium, fluorine, mercury, lead, arsenic (III), and possibly Cr (VI) should be particularly monitored at these selected sites.

Current Status

Sources of Hazardous Elements in the Coal Fuel Cycle

Extraction, cleaning, transportation, storage, combustion or conversion, and ash disposal are the sources of trace elements and radionuclides in the coal fuel cycle (6). These contaminants may enter the atmosphere, landscape, and hydrosphere and, depending upon physical, chemical, and biological factors, enter food chains leading to man. Contaminants introduced into the atmosphere may reach man

Table 1. Average trace element concentration in coal by state^a

	Trace element concn, ppm												
	Northern Appalachian		Southern Appalachian				Eastern Interior			Powder River Region		Four Corners	
	W. Va.	Penn.	Eastern Ky.	Ala.	Va.	Tenn.	Ill.	Western Ky.	Ind.	Mont.	Wyo.	New Mexico	Ariz.
As	9	16	6	13	10	9	6	7	7	<6	1	2	2
Ba	77	70	79	110	99	120	49	44	31	380	170	270	39
Be	1.2	0.8	1.5	0.74	1.1	0.58	1.3	1.4	1.7	1.5	2.4	0.94	0.97
B	20	15	19	30	13	24	81	70	85	60	36	43	49
Cd	—	—	—	—	—	—	2.9	—	—	<0.1	0.46	<2.6	<0.54
Cr	19	24	19	19	20	19	29	18	19	3	5.8	11	9.7
Co	17	18	15	18	14	13	15	16	24	7.7	5.2	15	—
Cu	11	13	11	14	13	11	8.3	8.8	9.7	3.2	4.4	5.9	4.9
F	70	90	30	90	50	120	59	—	50	70	160	160	70
Pb	4.9	5.2	4	3.7	6.1	4.9	33	6.4	7.2	4.8	0.61	4.7	3.9
Li	44	64	78	75	34	36	45	16	24	27	19	16	19
Mn	21	21	26	19	42	23	73	19	26	57	14	19	9.7
Hg	0.12	0.20	—	—	—	—	0.18	—	0.08	0.07	0.05	0.08	0.05
Mo	6.2	9.8	5.2	11	8.3	7.8	8.8	7.4	5.2	4.8	2.2	2.0	0.97
Ni	18	20	16	17	22	16	25	16	33	3.3	4.1	8.1	4.9
Se	3.4	3.7	3.1	5.1	4.4	4.9	2	3.1	4	3	0.8	2.0	2.1
Te	—	—	—	—	—	—	—	—	—	—	0.025	0.03	<0.02
Tl	—	—	—	—	—	—	—	—	—	—	0.4	0.24	<0.2
Sn	1.5	1.1	4.6	2.2	2.3	1.8	2.6	2.5	0.74	1.1	1.4	1.9	0.97
V	30	33	29	31	33	34	35	32	35	12	15	25	9.7
Zn	17	22	15	22	23	23	140	48	73	42	37	19	9.7
Zr	63	68	60	56	44	45	88	77	100	77	39	110	39
U													
(range, not avg.)	<10-30	20-190	10	—	<10	—	<10-80	—	10	10-340	10-1000	10-6200	—

^aSource: Dvorak (6).

and other animals through inhalation and plants through fumigation while those entering the aquatic and terrestrial environments reach plants and animals through root uptake and ingestion. Trace elements and radionuclides in U.S. coals have been widely studied (4, 7, 8). Concentrations of trace elements in coal are sometimes difficult to determine accurately and tend to vary considerably among different coal types (Table 1). Thus, it is not appropriate to compute a national average for each trace element in coal (9). Radioactive elements in coal, ²³⁵U, ²³⁸U, ²³²Th, and associated daughter products, are also variable (Table 2), but values of 1 ppm U and 2 ppm Th have been assumed to be reasonable national averages (7, 10).

Coal extraction, both surface and subsurface, produces solid wastes and acid or alkaline mine drainage which contain trace elements and radionuclides that are transported to aquatic environments (6). Acid mine drainage from inactive underground mines is difficult to control and is the greatest single source of drainage in the eastern United States (11). The acidic nature of acid mine drainage tends to hold metal ions in solution and

promotes transport to surface and ground waters. Trace elements of concern include Al, As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, and Zn (12). In western coal provinces acid formation is almost nonexistent, but transport of alkaline drainage containing soluble salts from mine spoils to receiving waters is one of the most significant water quality problems in those regions (13).

Coal processing or cleaning produces coal fines and rock material. The refuse is separated into gob (course-boulder to pebble-size rock) and slurry (clay-sized particles of coal fines). Problems associated with coal cleaning refuse are generally limited to the coal regions of central interior and eastern provinces (6). Acid drainage or runoff of refuse piles are sources of trace elements to terrestrial and aquatic environments.

Large coal-fired electricity-generating stations [≥ 1000 MW(e)] require coal storage in order to maintain a continuous supply between shipments. Permanent coal stockpiles for a typical 1000 MW (e) plant may vary from 500 to 900 thousand short tons and require from 1 to 2.5 hectares (6). Suspension of coal dusts and infiltration and runoff waters are

Table 2. Range of uranium and thorium concentrations and geometric means (expected values) for coal samples taken from various regions of the United States.^a

Region	Coal	Number of samples	Uranium concentration (ppm) ^b		Thorium concentration (ppm) ^b	
			Range	Geometric mean	Range	Geometric mean
Pennsylvania	Anthracite	53	0.3-25.2	1.2	2.8-14.4	4.7
Appalachia	Bituminous	331	<0.2-10.5	1.0	2.2-47.8	2.8
Interior	Bituminous	143	0.2-43	1.4	<3-79	1.6
Northern Great Plains	Subbituminous, lignite	93	<0.2-2.9	0.7	<2.0-8.0	2.4
Gulf	Lignite	34	0.5-16.7	2.4	<3.0-28.4	3.0
Rocky Mountain	Bituminous, subbituminous	134	<0.2-23.8	0.8	<3.0-34.8	2.0
Alaska	Subbituminous	18	0.4-5.2	1.0	<3.0-18	3.1

^aSource: McBride, (4).

^bThe arithmetic average concentrations of thorium and uranium for all coal samples and various ranks of coal for the whole United States are given in Table 3.

Table 3. Arithmetic averaged concentrations of uranium and thorium in coal for the whole U.S.

Coal rank	Samples	Thorium, ppm	Uranium, ppm
All coal	799	4.7	1.8
Anthracite	53	5.4	1.5
Bituminous	509	5.0	1.9
Subbituminous	183	3.3	1.3
Lignite	54	6.3	2.5

major trace element and radionuclide sources to the environment. Terrestrial effects are generally negligible except on areas immediately below and adjacent to the piles. Ground sealing prior to establishing the coal pile can reduce infiltration into ground water (14). Contamination of aquatic environments from runoff from coal piles is similar to but of lesser magnitude than that from acid mine drainage.

Coal combustion produces fly ash and slag or bottom ash as solid waste products. Slag is that portion of total ash which melts to a viscous fluid at combustion temperatures, and bottom ash is the remainder that does not melt and is too heavy to be entrained in flue gas. The amount of slag and bottom ash produced in combustion is a function of coal type and boiler design. Bottom ash is generally mixed with fly ash and pumped in a slurry to settling ponds or dewatered and transported to landfills. Settling ponds are sometimes lined with clay to reduce leachate movement into ground water (14). In the absence of liners, trace elements and radionuclides in leachates can move into underlying soil and ground water (15) and are subject to a variety of chemical, physical, and biological factors that govern their mobility and availability in the environment.

Trace elements in coal tend to partition or concentrate in certain phases during combustion. Klein et al. (16) categorized trace elements into three classes: (1) elements that are not volatilized in the combustion zone, but instead form a melt that becomes both fly ash and slag (Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Sm, Sr, Ta, Th, Ti); (2) elements that are volatilized on combustion, and condense or adsorb on the fly ash as the flue gas cools, leading to depletion from slag and concentration in the fly ash (As, Cd, Cu, Ga, Pb, Sb, Se, Zn); and (3) elements that remain almost completely in the gas phase (Hg, Se, Cl, Br). The elements Cr, Cs, Na, Ni, U, and V were intermediate in behavior and were placed between classes one and two. Following combustion, trace elements released to the atmosphere in association with particulates may be selectively adsorbed in different particle size ranges (17) and may be enriched on fly ash particle surfaces relative to the interior of the particle (18).

Coal gasification appears to be the only coal conversion technology that will be on-line by the year 2000 (19). Trace elements and radionuclides may be released to the environment from gasification primarily from noncombustible solid wastes that will be disposed of in landfills or slurry ponds. Atmospheric releases of volatile or hydride-forming species is a potential but undefined source of trace elements from gasification.

Environmental Transport

Before the effects of coal-derived trace contaminants on man and ecosystems can be evaluated, it is necessary to estimate the transport, transformation, and bioaccumulation of these contaminants as they move from the power plant to the receptor. In addition,

tion to determining routes of transport and transformation, rates for these processes also must be determined before we can predict environmental fate and levels of exposure. Information on the physical and chemical characteristics (e.g., particle size, solubility, and valence state) of materials released to the environment is a vital prerequisite to study of transport processes. The following discussions of environmental transport are based in part on an analysis by Crawford et al. (20).

Atmospheric Transport and Dispersion. Seasonal and annual pollutant concentration fields in the atmosphere can be calculated with reasonable accuracy (within a factor of 2 to 3) at distances of up to 10 km from the effluent source if attention is restricted to simple terrain types and typical daytime atmospheric stability categories (21, 22). Probability distributions of hourly concentrations from seasonal and annual data can also be calculated with similar accuracy. At longer distances, models can be formulated to account for transport and, to a lesser extent, dispersion. The data required for distances > 10 km are not readily available however, and the models have not been thoroughly validated.

Wet Deposition. Precipitation scavenging of particles and gases has been measured in the neighborhood of coal-fired power plants, and the experimental results are fairly well modelled theoretically, at least for estimates of total mass scavenged. Details of the removal as a function of particle size, however, remain in a primitive state.

To estimate precipitation scavenging on a total-mass basis, two approaches are available. In one, a scavenging rate coefficient which accounts for the particle size of the trace contaminant is used (23). Estimates of the removal rate for snow scavenging are also available (24). In the second approach, a wet deposition velocity is derived using washout ratio data (23, 25). These washout ratios show relatively little variation for the trace contaminants and using them, one can define a convenient wet deposition velocity for typical annual rainfall amounts in the northeastern United States (~ 100 cm/yr) as approximately 1 cm/sec for trace metals of interest. It is appropriate to use the washout ratio for long-term-average estimates; the scavenging rate approach should be used for short-term estimates. Methods for including precipitation scavenging in diffusion calculations are available (26).

Dry Deposition and Resuspension. Dry deposition of particles to smooth surfaces as a function of particle size and turbulence intensity is fairly well known from wind tunnel studies, and theoretical analyses demonstrate a fair understanding of the processes involved. Dry deposition of submicron

particles to real surfaces (e.g., grass, shrubs, trees, lakes, etc.) is an unknown. Best available "guesstimates" suggest using a dry deposition velocity for all particles to all real surfaces: $v_d = 1$ cm/sec. However, different values are obtained for different atmospheric conditions and surface roughnesses.

Resuspension of particles has only recently become of interest in the atmospheric sciences, although much useful information is available in the soil and agricultural science literature. However, in these fields, the emphasis has been more on wind erosion than on the resuspension of submicron particles which is of dominant interest for evaluation of inhalation health effects. In this regard, attention must be paid to bounce-off during the deposition process (27), resuspension by rain splashing (28), and freeing of submicron particles from supermicron particles during dissolution in water (29) and by bombardment of larger particles (30).

Water and Solutes Transport in Soils. For sites downwind from a coal-burning power plant where trace elements or their complexes reach the soil surface by wet or dry deposition from the atmosphere, the most important determinants of their environmental fate are likely to be sorption and desorption on soil particles at the soil surface and the subsequent mobility of these trace elements as a result of soil erosion caused by both wind and water.

The transport of coal-derived trace elements and radionuclides within the soil depends on water movement and chemical reactions within the soil profile. The use of available techniques for predicting and monitoring movements of soil water in the vicinity of a coal-burning power plant depends upon accurate field determinations of the horizontal gradients in the water table head and hydraulic conductivity at the site in question.

When the movement of water through the soil has been characterized, information about chemical and physical reactions which occur simultaneously with the soil water behavior is required in order to predict the retention and transport of trace elements in the soil. Processes of sorption and desorption between the organic and inorganic solid phases of the soil are usually strong and can prevent rapid leaching of these elements into surface and ground waters. On the other hand, some chemical forms of trace substances are repelled from the solid phases and may leach readily with the water. Many reactions in the soil are Eh- and pH-dependent. Some contaminants present in coal waste material may interact with the soil exchange complex and may be far more soluble than one would expect from a simple water extract; others, although highly soluble in water extracts, may precipitate with materials present in the soil.

Processes of erosion and sedimentation represent large portions of the mass flow and should be included in conceptual models and measurements of hydrologic transport (31).

When the kinds of information described above are available, estimates of the migration of trace elements from land disposal sites that receive slag, scrubber effluent, fly ash, and bottom ash can be made. Vertical and horizontal movements in both the water-saturated and unsaturated zones of the soil can be estimated from the disposal site to the receiving waters.

Transport in Aquatic Environments. Trace contaminants that enter the aquatic environment are usually rapidly taken up through adsorption by components having the highest surface-to-volume ratios, primarily the small suspended solids and sediments, and absorption by similar sized microbiota. The largest reservoir of trace contaminants is the bottom sediment. Here a complex association of inorganic and organic components similar to those found in soil form a system which governs the availability of contaminants to the rest of the ecosystem. The physical factors pH, Eh, pore space, and chemical transformations influence the retention/mobility of contaminants in aquatic systems. Similarly, biological transformations play a key role in aquatic transport and distribution. In streams, contaminants may be transported downstream in dissolved form or in association with suspended sediments, ultimately to be deposited into lake sediments or taken up in food chains and cycled among various biological components.

Biological Transport and Transformation

At nearly every point along the physical transport pathways in both aquatic and terrestrial environments, opportunities exist for interactions with the biotic components. Organisms can absorb hazardous elements from their physical environment and dilute, concentrate, transform, and immobilize these materials which may or may not affect ultimate contaminant toxicity. Biological transport plays a major role in determining exposure of organisms to contaminants, but only a minor role in material transport through the environment with little or no effect on contaminant inventory.

Food Chains. Primary producers generally serve as the base of food chains and may accumulate elements through roots (plant uptake), leaves (foliar absorption), absorption through cell walls in aquatic plants, and adsorption on external surfaces. Elements physiologically fixed in plant tissues as opposed to those on plant surfaces or in intracellular

water streams may have different properties and behave differently when ingested by consumers (32). Elements may return to the physical environment through death and leaching, or they may enter food chains through ingestion by consumers. Following ingestion, elements may pass straight through the digestive tract or they may be assimilated. Assimilation rates may vary from < 1% per day for certain elements up to 100% per day for others depending upon both animal and element species in question (33). Following assimilation, elements are distributed in various tissues at various rates in the consumer's body. Cadmium, for example, tends to accumulate in renal tissues and methylmercury in the central nervous system. Other elements, particularly heavy metals and transuranics tend to be bone seekers. Elimination of elements from various tissues proceeds at various rates and results in release of the chemical into the digestive tract to be eliminated from the consumer through egestion. Consumers may die or they may be consumed by subsequent steps in a food chain. Compounding this simplified picture of a food chain are the biotransformations that may occur, changing the structure and biological activity of chemicals, and the question of direct uptake from surrounding air (inhalation) and water (gill and epidermal absorption).

Soils tend to be the sink for most chemical contaminants released to terrestrial environments. In addition to water relations and soil sorption-desorption phenomena, microbial interactions and root uptake play major roles in transport and distribution of chemicals in terrestrial systems. Microbes can operate in both aerobic and anaerobic environments and have profound effects on element mobility. From the soil-soil-water continuum plants may accumulate elements through root uptake, a process of both active and passive nature. Plant roots show preferential uptake of particular elements and can exclude others at membrane boundaries. Heavy metals entering plant roots are believed to be chelated prior to their movement in xylem and phloem streams (34).

Typically, aquatic food webs are more complex than those found in terrestrial systems. Adsorption-desorption of elements on suspended sediments and direct absorption by organisms from water are added parameters in aquatic systems. Chemical contaminants generally reach aquatic environments by direct deposition (disposal), runoff from land surfaces, and leachates in ground water. Chemical and physical reactions among sediments, interstitial water, the water column, and decomposers can affect the routes and rates of transfer as well as the chemical and biological properties of contaminants. Aquatic

plants obtain elements from the water column through absorption although surface adsorption is important because of high surface-to-volume ratios found in algae and other phytoplankton. Decomposers may act upon organic matter in anaerobic sediments resulting in release of heavy metals to interstitial waters and their subsequent diffusion into the overlying water mass. Because of the chemical and biological activity present, sediments may act as sources and sinks of chemical contaminants in the aquatic environments.

Biological Concentration. The ability of animals and plants to accumulate chemical contaminants to levels above those of their food source or substrate is a common biological phenomenon. Trace elements, including heavy metals and radionuclides, are accumulated to varying degrees (35-37). In aquatic systems, water is typically the reference point, while soil serves a similar role in terrestrial systems. Biological concentration of elements is governed by the amount of element present in the diet or surrounding environment, the chemical and physical forms of the element which determine its biological availability, the quantity of food consumed containing the element, the degree of assimilation of the element through cellular barriers (i.e., cuticle, lung, digestive tract, gills, etc.), and the extent of retention in the organism's tissues. Biological concentration occurs with natural elements for cellular maintenance and growth. It can also occur with hazardous elements when there is a strong chemical or physical resemblance to a common element or molecule which is necessary for everyday life processes (38).

Due to the variations that exist in the factors governing biological concentration among different environments and species as well as within one species in a particular environment, it is not true that because biomagnification occurs at one step in a food chain, it will also occur in subsequent steps.

Biological concentration factors for hazardous elements (Table 4) may vary over many orders of magnitude (10^{-3} to 10^5) in aquatic and terrestrial environments (36, 37, 39). Typically, biomagnification is greatest in aquatic environments where surface-to-volume ratios are greatest and where adsorption may overshadow absorption in relative importance. Bioconcentration factors for trace elements in terrestrial environments are generally less than unity with some exceptions.

Biological Transformations. Trace elements and radionuclides introduced into the environment are subject to biochemical interactions typically with microorganisms in soils and sediments although there are some biochemical transformation of hazardous chemicals in higher organisms. Microor-

ganisms are very versatile in their ability to chemically interact with natural and synthetic chemicals (41, 42).

The biochemical process of methylation of heavy metals and metalloids has received considerable attention in recent years although the reaction was first observed with arsenic in the late 1930's (43). Methylation is believed to be a detoxification mechanism for converting toxic ions to a more volatile form that will be released to the atmosphere (44). Several microbial species are capable of performing this transformation in soils and sediments under both aerobic and anaerobic conditions. Methylated forms of trace metals are frequently more toxic and are more readily absorbed by higher organisms than are inorganic forms. Methylation of mercury by microbes in marine and freshwater sediments is the best documented case of this type of biological transformation (35). Arsenic, selenium, lead, and tin are examples of other toxic elements that undergo methylation (45).

Higher organisms, including man, are capable of affecting biotransformations of hazardous chemicals. Reactions of Cd and metallothioneine in retention of this element in renal tissues are well documented by Friberg et al. (46).

Biotransformations of hazardous chemicals in the environment are particularly important in determining effects on man and other organisms because the molecular form and biochemistry of these transformed chemicals determine their availability, persistence, bioaccumulation, and toxicity.

Synergisms and Antagonisms. The combined action of two different chemicals may be greater than or less than the sum of the independent actions of each material. If chemical effects are simply additive, the increase is a simple algebraic addition. If the effect is greater than a simple algebraic addition, then synergism or potentiation has occurred. If the effect is less, antagonism exists. In the case of additive effects, the two compounds have the same points of attack. In potentiation, one compound usually acts on the metabolism of the second compound. The concept of synergism or potentiation covers both increases in usual effects of toxic compounds and production of lesions not observed by the action of either toxic compound alone (47). Synergisms and antagonisms are important in systems receiving multiple inputs of trace contaminants (i.e., aquatic ecosystems and ground water).

Ecological Effects

Ecological effects of hazardous elements have received increasing attention in recent years (6, 48, 49),

Table 4. Biological concentration factors for selected trace elements in aquatic and terrestrial environments.^a

	Biological concentration factor ^b				
	As	Cd	Hg	Pb	Zn
Aquatic					
Water	1	1	1	1	1
Plants	170	1000	1000	200	1000
Invertebrates	330	2000	100,000	100	10,000
Fish	330	200	1000	300	1000
Terrestrial					
Soil	1	1	1	1	1
Plants	0.01	0.3	0.4	0.07	0.4
Invertebrates	0.01	17		0.02	8
Mammals	0.001	0.008	5	0.001	0.6
Birds	0.001		50	0.001	

^aSource: Van Hook (40).

^bRatio of concentration in organism to concentration in substrate.

although most of this attention is focused on atmospheric releases of particulates and associated trace elements. Only recently have the problems associated with ground water contamination from ash disposal come to light (3, 15) although there has been considerable work with acid mine drainage and the hazardous elements contained therein (6). Similarly, coal-derived radionuclide impacts have been addressed from the human health point of view (4, 50), but insufficient data exist to evaluate the potential impact in natural ecosystems. The following discussions are based primarily on the work of Jones et al. (49) with supplemental information added where appropriate.

Coal Extraction, Cleaning, and Storage. Effects of hazardous elements from extraction on aquatic ecosystems will result primarily from acid mine drainage and erosion-induced siltation (51). Historically, these effects have been severe throughout eastern coal regions. The recently passed Surface Mining and Reclamation Act of 1977 should definitely improve this situation. Effects include decreased productivity and diversity, temporally and spatially altered species composition, altered species composition, and, in heavily polluted systems, absence of life. Factors which influence the effects of acid mine drainage and associated hazardous elements include degree of effluent dilution in receiving waters, the presence of other pollutants including sewage and industrial wastes, chemical states of metals in natural waters, pH, temperature, organic matter content, and synergisms (52). Western coals generally lack acid-forming substances (i.e., pyrites) which, along with the alkaline nature of western soils and overburden, suggests that acid mine drainage should be minimal in western coal regions. Increased salinity of surface and ground

waters in western coal regions appears to be due to soluble salts in mine spoils (53). Surface coal extraction can also affect ground water resources. Ground water aquifers are commonly intercepted during overburden removal with subsequent effects on ground water flow and quality. Hazardous elements may enter these disturbed aquifers and be mobilized and leached into surface waters.

Ecological effects of coal cleaning and storage are similar in nature but lesser in magnitude to those associated with acid mine drainage from coal extraction. Acid drainage or runoff from refuse piles may affect terrestrial and aquatic systems by lowering pH. Soils surrounding the refuse piles may accumulate potentially toxic levels of trace elements or radionuclides leached from the refuse by acid water. Aquatic environments adjacent to refuse piles can be severely impacted through sedimentation of fines and associated elements (6). The major long-term impact to terrestrial systems will probably be that the disposal area can only be returned to limited land uses (i.e., wildlife cover, recreation).

Coal pile runoff and leachates contain coal fines, hazardous elements, and humic acids and may be acidic. Terrestrial effects are limited to land under and immediately adjacent to coal piles while aquatic effects including elevated element concentrations and suspended solids will be more widespread. In arid environments, or during dry spells in other areas, fugitive dusts from coal and refuse piles may be suspended in the atmosphere and are subject to deposition on vegetation surfaces and inhalation by animals.

Coal Combustion — Solid Wastes. Combustion of coal results in solid wastes including precipitated fly ash, bottom ash, slag, and SO_x scrubber sludges which require onsite disposal, and gaseous and par-

ticulate emissions that pass through emission control devices and are released through stacks to the atmosphere. Currently, about 92% of the particulate material produced in utility boilers is removed with electrostatic precipitators (54). Fly ash, bottom ash, and slag all contain trace and radioactive elements, but the exact composition can vary widely depending on coal geology and boiler operating conditions. Elements tend to partition themselves into different ash components as has been discussed earlier. Studies of migration of trace elements from ash pond leachates through soils have produced variable results depending on coal type, operating conditions, and ash disposal sites. One study suggests no migration into ground water (55), whereas other investigators (15) indicate that trace metals are released to ground water at generally low concentrations, with attenuation occurring very close to the disposal site. While this may tend to minimize ground water contamination, it does not prevent uptake by plants whose roots penetrate the new water table created by the presence of the ash pond. Water and solutes will move upward and laterally through the soil from the new water table when soil surface evaporation and plant transpiration exceed rainfall infiltration. Accumulated hazardous elements may be toxic to the vegetation, or they may simply be stored and then become toxic to animals which consume the vegetation.

Aquatic environments receive trace elements and radionuclides from ash disposal through ground water (minimal) and direct runoff from settling basins. Direct runoff may contain dissolved and suspended materials which may or may not be available chemically to the biota. EPA guidelines call for application of BACT (best available control technology) to waste water effluents by 1983. Currently, best practicable control technology is applied at varying levels of success. At least 30 trace elements have been identified in measurable quantities in coal ash and a number of these are toxic to aquatic organisms at either the initial concentration or following biological transformation and/or concentration (56). Concentrations of radium, thorium, and uranium have been reported in fly ash (50), but there are insufficient data to assess the effects of these radionuclides or their daughter products on aquatic or terrestrial ecosystems from ash disposal sites. These data are particularly important considering that about 92% of the ash produced in coal combustion is placed in settling ponds and landfills. There are few data on the effects of trace elements on surface waters, but a study by Holland et al. (55) demonstrated concentrations of B, Ba, Cr, Hg, and Se in ash leachates exceeding federal surface water

standards for these elements. Results from this study varied from sample to sample and care must be exercised in generalizing to new situations.

To understand the effects of coal-fired steam-plant-derived elements on the aquatic system, it is necessary to quantify discharge of these elements. Calculations reported by Vaughan et al. (48) and Dvorak et al. (6) indicate that the atmospheric deposition of elements derived from coal combustion should exert a minimal influence on the chemical composition of lakes and rivers. The only elements that could be elevated were Hg, Cu, Sn, and Mo. This conclusion was reached despite the use of maximum transfer rates of fly ash deposited on soil and its migration to the drainage streams in the hypothetical watershed. An important additional consideration, however, is the impact of slag and fly ash discharges into the aqueous environment. The basis for this concern is that approximately 32×10^6 tons of fly ash with elevated levels of toxic elements is annually discharged into settling basins situated in close proximity to many coal-fired steam plants (57). Because it is known that many elements are leached from the fly ash (15), it is important to determine the mobilization potential of toxic metals from fly ash settling basins to the nation's surface and subsurface waters.

To obtain a better understanding of this mobilization potential, Klein et al. (58) calculated the quantity of elements that were annually discharged prior to 1975 in slag and fly ash to settling ponds and compared these values with data on natural weathering. Results of these comparisons indicate that except for Br, which is almost exclusively emitted as a vapor, the discharge into ash settling basins accounts for more than 1% of the elements mobilized by weathering. Elements such as As, Cd, Co, Cu, Fe, Mo, Ni, Pb, Sc, Se, U, and Zn all exhibit mobilization rates that are larger than 10% of the weathering rate, while rates for Mo, Se, and U are comparable to natural rates. Application of this analysis to more recent information (6, 7, 19) on coal combustion (6.8×10^8 t/yr) and on Cd and Hg concentrations in coal (0.5 and 0.2 $\mu\text{g/g}$, respectively), in soil (0.2 and 0.03 $\mu\text{g/g}$, respectively), and in water (0.1 and 0.07 $\mu\text{g/l}$, respectively), indicates that these elements are currently mobilized in coal combustion at rates equivalent to their natural weathering rates. Cadmium releases are predominantly associated with precipitated fly ash in settling ponds and landfills whereas the majority of the Hg exists in the plant stack with only about 10% going into solid waste disposal sites. Due to these considerations, it would be appropriate to investigate the regional effects of these fly ash-derived elements; that is, do the ele-

ments effectively remain in the settling basins or are they injected into the nation's waterways. Until such evaluations have been made, it will be impossible to predict, in a quantitative manner, whether coal-fired steam plants will exert any modification on the chemical composition of the nation's waterways.

The very high pH encountered in ash settling basins may influence the behavior of trace elements if this pH influence extends beyond the confines of the ash settling basin (i.e., into subsurface and surface waters). This high pH results from the hydrolysis of alkali and alkaline earths and may often exceed 11. In most ash settling basins it appears that atmospheric CO₂ diffusion into the water is not rapid enough to lower the pH. One would predict that many metals would precipitate either as hydroxides or by coprecipitation (e.g., calcium carbonate). If settling is not complete, however, particulate matter containing elevated levels of metal carbonates, hydroxides, or sulfates could reach the discharge waters. Upon reaching lower pH discharge waters, these particulates might redissolve, thus producing an increase in available metals to aquatic plants and organisms. Alternatively, high pH effluent waters might produce a beneficial effect, in terms of metal removal, on lakes and rivers with low buffering capacity. The change in pH, however, might also affect the plants and organisms in the receiving waters. These implications should be considered before the impact of coal-fired steam plants on the aquatic ecosystem can be evaluated.

Coal Combustion — Atmospheric Emissions. Coal combustion emissions released through stacks to the atmosphere can be transported over considerable distances (see Environmental Transport section). The ecological effect of hazardous elements associated with these emissions will vary as a function of chemical and physical form of the element, the site of deposition, and the amount of material deposited. As pointed out earlier, volatile elements in coal include As, Be, Cd, F, Hg, Se, Sb, Br, Cl, Cu, Ga, I, Ir, Mo, Pb, and Zn (16, 58, 59). All pose some degree of potential hazard to man and might adversely impact the environment at some threshold concentration. The amounts and forms of these elements that exit the stack of a coal-fired power plant are largely unknown and probably vary between plants, depending on the coal source and pollution control technology. The effect of electrostatic precipitators in reducing these emissions is likewise unclear, although some consider a high percentage of these elements should be found in the particulate of the precipitators. Natusch et al. (17) reported that As, Sb, Cd, Pb, Se, and Tl preferentially concentrated on particulates in the respirable range, a large part of which is not

removed by existing high-efficiency precipitators.

Cannon and Swanson (60) found that concentrations of trace elements in soils (i.e., Hg, As, Sc, Te, Cd, Be, and Pb) dropped rapidly with distance from the Four Corners Power Plant, and concentrations were lower than those for average soils at distances beyond 3 km. Vegetation within 3 km of the plant had not, within the time span of their study, accumulated significant quantities of these potentially toxic trace elements. The authors concluded that with the installation of more efficient precipitators, the atmospheric trace element emissions from this plant would not be considered harmful to the biota. Horton et al. (61) measured the concentrations of 29 trace elements in soils and vegetation within approximately 11 km of a coal-fired power plant in South Carolina that had been operating since 1952. With the possible exception of Se (in soils) and Mn (in ground water), none of the trace elements released to the atmosphere from the plant contributed significantly to the concentrations of the elements in the immediate environment. No enrichment or depletion of trace elements was detected in soils in the vicinity of Allen Steam Plant near Memphis, Tennessee, but the soil was under the influence of agricultural practices (62). Klein and Russell (63), however, reported that sandy soils on the eastern shore of Lake Michigan near a power plant were found to be enriched in Ag, Cd, Cs, Cr, Cu, Fe, Hg, Ni, Ti, and Zn. Vegetation was enriched in Cd, Fe, Ni, and Zn.

Vaughan et al. (48) modeled the cumulative impacts of trace element emissions over a 40-year period from a hypothetical 1400-MW(e) power plant in the western United States burning representative western coal. Their model predicted that four trace elements, Cd, Mo, Cu, and W, might accumulate (by at least a factor of two) in growing plants. However, they did not have sufficient data to make predictions for a number of trace elements such as Ga, Ce, Ra, Te, Th, Tl, and V. In a similar analysis on a hypothetical 1000-MW(e) power plant, Dvorak et al. (6) concluded that even when the atmospheric particulate emission rate is at the maximum allowed by NSPS (0.1 lb/10⁶ BTU), the impacts to vegetation are expected to be minimal. These authors point out Cd and Se as having the greatest potential for adversely affecting animals.

A number of the trace elements (i.e., Fe, Cl, B, Mn, Zn, Cu, Mo, Co, Se, I, Cr, Sn, V, F, Si, and Ni) are essential at low concentrations for either plant or animal life but are toxic at higher concentrations (64). Some of the nonessential trace elements, such as Cd and Hg and essential Zn and Cu in marine environments, are toxic to sensitive species in con-

Table 5. Potential toxicity of trace elements in coal.^a

Element	Terrestrial		Aquatic	Comments
	Plant	Animal		
As	Low	Low	Low	Know enough on toxicity for terrestrial ecosystems, in some instances may be beneficial
B	High	Medium	Low ^b	
Be	Medium	High	High ^b	
Bi	Medium	Low	Low ^b	Speciation important
Cd	High	High	High	
Co	High	Medium	High	Cr ⁺⁶ very toxic — need to know speciation
Cr	High	Medium	Medium	
Cu	High	Medium	High	
F	High	High	Low	Complexion in soil reduces toxicity, in some instances may be beneficial
Hg	Medium	High ^b	High	
Mn	Low	Low	Low	Enriched in plants, toxicity in food cycle
Mo	Low	Medium	Low	
Ni	High	High	Medium	Potential for net beneficial effect
Pb	Low	Medium	Medium	
Sb	Medium	High ^b	Low ^b	High enrichment in plants — beneficial or adverse effects
Se	Medium	High	Low ^b	
Sn	Low	Low	Low	Very mobile in plants
Ti	Low	Low ^b	Medium ^b	
Tl	High	High	Medium ^b	Potential for net beneficial effect
V	High	Low ^b	Medium ^b	
W	Medium	Medium ^b	Low ^b	Potential for net beneficial effect
Zn	Low	Medium	Medium	

^aSource: Jones et al. (49).^bUncertain.

centrations only slightly above those occurring naturally (65). Biotic dose-response relationships for trace elements are at best poorly defined, and almost nonexistent for those species comprising natural ecosystems. The effect of high concentrations of trace elements is ultimately a function of the tolerance of individual plants or animals.

Jones et al. (49) have classified the potential toxicity of various trace elements in coal into three main categories — high, medium, and low — for terrestrial and aquatic life (Table 5). The authors consider this information to be a "best estimate" based on their collective experience, knowledge, and intuition. It should be pointed out that the impact on the overall soil-water-plant system is also a function of the chemical state of the trace element which impacted the system and its interaction with the local environment. This interaction will determine the trace element availability and, therefore, the fraction of the total trace element concentration that can affect growth.

Soils represent the principal repository of trace contaminants from fossil-fuel combustion over geologic time. Therefore, the soil is the principal medium for long-term exposure of coal effluents to terrestrial plants and animals. The effects of trace

metals on important soil microbial processes and the role of soil microorganisms in influencing the long-term availability of trace metals to plants are largely unknown. Inhibition of microbial processes may have important secondary effects on the ecosystem. Furthermore, microorganisms exist predominately in the immediate vicinity of the soil particle where trace metal concentrations are highest. Microorganisms thus have the potential for alteration of the form of the metal through interaction with normal metabolites or by direct conversion processes.

Trace elements have long been known to affect plants. In the case of the essential trace nutrients (Fe, Cl, B, Mn, Zn, Cu, and Mo), a broad range of possible responses exists, ranging from deficiency to toxicity. In the case of the nonessential trace elements, only the no-effect (tolerant) and toxic portions of the dose-response curve are expressed. Under natural conditions, there are examples of plants growing under both deficient and toxic conditions. Whether the trace element emissions from coal-fired power plants can enhance or inhibit plant growth depends on whether these elements will have a significant effect on naturally occurring concentrations. There is no reason to expect acute effects on plants from atmospheric trace element emissions

from coal combustion systems and little reason to expect acute effects to aquatic systems. The potential for chronic toxicity is relatively low except for particularly toxic elements such as F (66) or in local areas already enriched with a particular element.

Some trace elements combine the properties of high toxicity, a potential for bioaccumulation in food webs, and persistence in the environment. Many of these substances are toxic in sensitive animal species at concentrations that are only slightly above naturally occurring levels (64, 65). Higher trophic levels, as a result of bioaccumulation, may be affected at "ambient" concentrations that would not be expected to affect plants. Even with these reservations, it is probable that trace elements in emissions have little or no discernible effect on animals. Effects would seem possible only if the emissions that are currently accepted are in error by an order of magnitude. Sublethal, chronic, or synergistic effects of trace contaminants that may be of significance in natural terrestrial animal populations have received little attention (6). However, because some of the trace elements have been reported to adversely affect soil/litter communities (67) and possibly alter primary productivity (67, 68), and, in turn, secondary productivity, potential long-term impacts on ecosystems could occur if trace elements emitted from coal combustion persist or accumulate in ecosystems to toxic levels.

Health Effects

Any assessment of possible health effects from coal combustion contaminants requires, *inter alia*, definition and quantitation of source and transport terms. Given information on "what" and "how much" can be breathed and ingested, an evaluation of the human exposure and intake estimations can proceed utilizing background, dietary, occupational, experimental, and environmental information, provided these data exist. A number of reports have been published on health aspects of trace contaminants from coal combustion (1, 4, 6, 48, 69-71). These reports have been utilized in developing the following discussion.

Physiological and pathological responses of a population to radionuclides and trace elements from coal will reflect the individual's ability to respond and the duration of exposure. Short-term adverse effects will be manifest in those subgroups more sensitive to the pollutant (i.e., children, aged, infirm) as an increased incidence of respiratory diseases, aggravation of preexisting chronic cardiopulmonary diseases, and premature death. Chronic exposure on the other hand may result in an increased incidence of respiratory diseases and cancer in the total popu-

lation. The major health effects of concern relative to coal combustion products include physiological irritation, direct toxicity, carcinogenesis, and physical synergisms. The following discussions center primarily around atmospheric emissions from coal combustion with much less emphasis on solid wastes (ash and slag). This is due to a virtual absence of information about the contribution of coal-ash-derived hazardous elements to the ambient levels in man's environment or their subsequent contamination of food or drinking water.

Electrostatic precipitators are typically more efficient for larger diameter particles in flue gas. Particulates existing in the power plant stack are generally in the respirable size class. The toxic effect produced by respirable particles depends on the chemical species they contain. Smaller particles tend to be more toxic than larger ones due to size and selective adsorption of heavy metals (17). Submicron fly ash particles represent a double threat to human health (6); they reach the pulmonary region and remain there for extended time periods, and they can deliver a given concentration of hazardous element to a very localized area thereby magnifying the effect.

Coal Extraction, Cleaning, and Storage. Human health effects of hazardous elements associated with coal extraction, cleaning, and storage include inhalation of coal dusts which may contribute to development of black lung (coal worker's pneumoconiosis) (72), and ingestion of trace elements and radionuclides from drinking water contaminated by acid mine drainage. Acid mine drainage impacts are generally more widespread, and in communities without alternate sources of water, or undeveloped water sources, these impacts can represent a severe problem (6). Runoff from coal piles and coal-cleaning wastes contribute to water quality degradation but on a much smaller scale than acid mine drainage. Atmospheric loading of coal particulates arises through resuspension of coal fines from storage piles and from accidental ignition of both coal piles and coal-cleaning waste piles.

Coal Combustion. The radiological impact of coal-fired power plants appears to be adequately evaluated for atmospheric releases (4, 73). McBride et al. (4) estimated annual release rates for a 1000-MW(e) power plant burning coal at a rate of approximately 100 tons/hr, containing 1 ppm of uranium and 2 ppm of thorium (both assumed to be in secular equilibrium), and releasing 1% of its fly ash to the atmosphere (the average ash release for 1972 was 8%). Under these conditions, ^{228}Th , ^{232}Th , ^{224}Ra , and ^{212}Pb each contribute approximately 5×10^{-3} Ci/yr; ^{238}U , ^{234}U , ^{230}Th , ^{234}Th , ^{226}Ra , ^{210}Pb , ^{210}Po , ^{210}Bi each contribute approximately 8×10^{-4} Ci/yr;

and ^{220}Rn and ^{222}Rn together account for approximately 1.2 Ci/yr. These release rates were then applied to a population of ~ 3.5 million persons living within a 90-km radius of the power plant. The dose calculations took into account doses from immersion, contaminated ground surface, inhalation, and ingestion, wherein all doses from food and water were derived from within the 90-km radius of the plant (74, 75).

The following population dose commitments were determined: 10 to 25 man-rem/yr whole body dose and approximately 100 to 240 man-rem/yr bone dose. The corresponding average individual dose commitments were 0.003 to 0.007 mrem/yr and 0.03 to 0.07 mrem/yr, respectively, where the ranges pertain to emission patterns from different stack heights (300-50 m). The maximum individual dose commitment at 500 m from the stack was 1.9 mrem/yr and was independent of stack height. The dose commitment is based largely on ^{226}Ra ingestion and essentially doubles if the U content of the coal is doubled. If bituminous coals are used, the U concentration is often as high as 20 parts per million, so this could increase both the release and dose commitment figures by an order of magnitude, assuming all other factors remain constant.

Of relevance are the data of Martin et al. (50), who measured downwind levels of U from a 1400-MW(e) coal-fired power plant and found fCi/m³ concentrations, implying daily intakes by humans would be of the order of a few femtocuries. Ambient air levels of approximately 400 aCi/m³ of U have been reported, indicating a concentration of about 2 pCi/g for atmospheric dust or approximately 2 ppm by weight, which is not greatly different from the U concentration in fly ash from an average anthracitic coal.

To compare the magnitude of the radiation dose from coal combustion emissions to that from natural background (76), it is useful to use dose-equivalent rates. On this basis, NCRP (76) indicates that the dose equivalent rate for ^{226}Ra from natural background is about 7 mrem/yr for bone and less than 1 mrem/yr for the whole body. The dose equivalent rate for the whole body from all natural radiation sources is 80 ± 40 mrem/yr; the corresponding coal combustion figure would be 7×10^{-3} mrem/yr. Radiation protection limits for whole body irradiation of individuals within a population are set at 500 mrem/yr with an average genetic dose limited to 170 mrem/yr (5 rem in 30 years). A proposed guideline would limit the whole body dose to members of the critical population to 5 mrem/yr from atmospheric releases.

The new EPA Primary Drinking Water Regulation for Radioactivity (40 CFR 141, 1975) limits the ^{226}Ra

and ^{228}Ra combined activity to 5 pCi/l., gross α activity to 15 pCi/l., and any combination of β - α whose concentrations produce a dose equivalent of 4 mrem/yr to the whole body. Whether any of these regulations might be exceeded in the immediate environs of a coal-fired power plant is uncertain. This uncertainty is due to a lack of information concerning the release of radionuclides from solid waste disposal sites which receive in addition to bottom ash and slag, the 92% of the fly ash from combustion that is removed from flue gas by electrostatic precipitators.

Morrow et al. (69) have made estimates of chemical toxicity of nonradioactive trace elements using maximal expected airborne levels 1 m above the ground associated with 0 to 15- μm diameter particles within a 20-km radius of a 1400-MW(e) coal-fired power plant with a plume height of 300 m [see Table 23 of Vaughan et al. (48)]. The predicted air concentrations resulting from their calculations, and presumably good to a factor of 3, were compared to ambient air concentrations, atmospheric standards for population exposures, reference man data for inhalation intakes, and occupational Threshold Limit Values (TLV). By this approach, generally accepted, safe ranges of atmospheric concentrations were established.

Results of their analysis revealed several uncertainties. Three elements [As (III), Cr (VI insol), and Ni carbonyl] are generally accepted as having potential carcinogenic importance, so the general approach used in this tabulation may be inappropriate. For Ni, As, and Cr, a critical question concerns the occurrence and magnitude of the carcinogenic forms of these elements, namely, As (III), Cr (VI insol), and nickel carbonyl, oxide, sulfide, and carbonate in coal combustion effluents. On the basis of the currently available information, Cr (VI) probably occurs; the nature of the nickel compounds is unknown, but the highly volatile carbonyl is assuredly absent from fly ash. For As, the expectation is good for both the III and V oxidation states, but no quantitative findings exist — only the indication that fly ash leachates contain both forms.

The reported teratogenic properties of certain Cd, Se, and Hg compounds, the mutagenic potential of certain Pb and Hg compounds, and the carcinogenic properties of Be and Se (77) are, in general, only demonstrable at high doses or under uncommon circumstances. Consequently they warrant no species concern at this time.

Information on the metallo-organic forms of Hg is lacking, as it is for other elements, but there is little likelihood that they occur in the emissions from coal combustion associated with particulate matter. Even if alkyl mercury were the singular form of Hg emit-

ted, its acceptable air concentration indicates that it probably would be unimportant toxicologically.

Because of the uncertainties in the assumptions and models used, the variability in the trace element composition of coal and in the naturally occurring levels at specific power plant sites, Be and F may constitute potential health problems in the immediate environment of coal power plants. Otherwise, the majority of the elemental concentrations calculated by Morrow et al. (69) appear to be one or more orders of magnitude below the "acceptable air concentrations."

Berry and Wallace (2) sampled the plants and soil around a coal-fired electric plant at Moapa, Nevada, burning approximately 100 tons of high ash coal per hour, and concluded that forage and milk from the area could become seriously contaminated if high arsenic coals (> 500 ppm) were used for several decades. Excessive Cd contamination of forage and dairy products also could be envisioned and some concern was expressed regarding F contamination. In other studies of coal power plants, some enrichment of trace elements (e.g., Hg, Sc, and Pb) in soil and plant life has been reported (60, 61). In the Four Corners study (60), Pb was found enriched in soils, but no toxic trace metals were found in excess of average soil values at a 3-km distance from the plant.

Comparisons of data from Vaughan et al. (48), Pinkerton et al. (78) and Bolton et al. (62) indicate that the soil build-up of trace metal contaminants will be slow, and allowing order-of-magnitude perturbations in depositions and soil conditions, one would not expect excessive bioaccumulation to occur in plants unless the bioavailability of exogenous fractions is orders of magnitude greater than that of typical soil. There is evidence that exogenous elements are more water soluble, implying greater bioavailability on the one hand and shorter soil retention times on the other. A potentially more important source of water and biotic contamination relates to slag and fly ash disposal. Ponding, ground burial, and other disposal techniques will lead to consequences of greatly different magnitude, and as pointed out earlier, very few data are available in this area. Thus, one of the greatest uncertainties in this health effects evaluation relates to the potential intake of heavy metal contaminants from water and food exposed to ash disposal effluents.

The first Food and Drug Administration Market Basket Survey (79) indicated that for some metals (e.g., Cd) the dietary intake levels are already approaching tolerable limits. The initial survey estimated the daily intake of five selected metals in $\mu\text{g}/\text{day}$ for a U.S. adolescent male as follows: As, 10.1; Cd, 51.2; Hg, 2.9; Pb, 60.4; and Se, 149. On the basis of the provisional WHO/FAO tolerated intake

limits for heavy metals by adults, the Market Basket Survey estimates for total Hg, Pb, and Cd intake are about 7, 14, and 75%, respectively, of the WHO/FAO limits. Cadmium has an unusually wide distribution in foodstuffs so that soil levels will be reflected generally in water, fruit, vegetables, meats, and dairy products. In addition, current mobilization of Cd and Hg through coal combustion is near the natural weathering rates for these elements and can be expected to increase with increased coal use.

Trace elements and radionuclides do not exist in isolation in the environment; they are released in association with major coal combustion contaminants (i.e., SO_x , NO_x , particulates) and may undergo chemical and physical transformations following discharge from power plant stacks. It is probably that such secondary chemical and physical interactions of the major and trace emissions, together with their physiologic interactions with tissues of exposed persons, may represent a most important aspect of the toxicology associated with combustion of coal. The two following examples illustrate the potential importance of such interactions.

Gaseous pollutants, including SO_x , NO_x , and O_3 , that increase the rate of cell proliferation of the tracheal-bronchial epithelium are highly suspect as important promoters or cofactors in the pathogenesis of lung cancer. In a survey of smelter workers exposed to As_2O_3 , the greatest excess of lung cancer was found in instances where there were accompanying exposures to high to moderate levels of SO_2 .

Oxidation of SO_2 to SO_4 does not always occur at perceptible rates in the atmosphere. Such oxidation appears to depend on the simultaneous presence of other factors — possibly hydrocarbons from automotive exhaust, or trace metals which may act catalytically. Adverse health effects in sensitive members of the population now appear to be better related to concentrations of sulfate aerosols than to SO_2 . Acidic sulfate aerosols have, theoretically, the potential to combine with heavy metal cations with unknown consequences. Thus a variety of synergistic actions from pollutant mixtures can be anticipated which will cause and/or exacerbate pulmonary dysfunction and chronic cardiopulmonary diseases.

Conclusions

Current Situation

Ultimately, trace elements from coal return to the soil or sediment systems whence they originally came. The trace elements and radionuclides in coal naturally occur in soils. Consequently, anthropogenic contributions of these elements in soils

are hard to distinguish from the large natural variability at distances of more than a few kilometers from a particular power plant. The chemical forms of trace contaminants are important determinants of transport and effects, yet most studies have focused on total elemental amounts or concentrations.

Basic concepts and models exist to describe the various pathways of environmental and biological transport. The rates of transport, however, are not well known, nor are input data on climatology, hydrology, and environmental chemistry available for most sites. It is important to obtain improved data on transport and transformation rates, particularly in relevant chemical and biological areas. These data will be essential in determining organism exposure to coal-derived hazardous elements.

Coal Extraction, Cleaning, and Storage. Acid mine drainage, particulate loading of the atmosphere from coal and refuse piles, and ground water contamination continue to be major problems associated with mining, processing, and storing coal. These problems are expected to improve as the new Surface Mining and Reclamation Act is implemented. Acid mine drainage from both surface and deep mines is prevalent in the Eastern and Interior Coal Provinces of the United States while alkaline mine drainage presents problems in the western provinces. Abandoned mines represent the major source of acid mine drainage in the eastern United States. Particulate loading of the atmosphere from the extraction-processing end of the coal fuel cycle occurs from suspension of coal fines and coal ash dusts from stable and burning coal and waste ash piles. Effects from these dusts and coal fines will presumably be confined to the immediate surroundings. Coal and refuse piles also serve as sources of hazardous elements in runoff and leachates which may enter the soil system and in some cases contaminate ground water. Generally, ground water contamination from these sources is minimal because of attenuation in soils. Effects of trace elements and radionuclides from coal extraction, cleaning, and storage are generally subtle when compared to the acid nature of drainage and runoff. Acute effects will be very difficult to sort out. Chronic effects may occur as a function of biological concentration and transformations that may render elements more hazardous because of amount, form, or location of accumulation.

Coal Combustion — Solid Wastes. Solid wastes from coal combustion consist of slag, bottom ash, precipitated fly ash, and scrubber sludge (if SO_x scrubbers are used). These wastes are typically stored wet in settling ponds or are dewatered and deposited in landfills. Settling ponds may also be mined following drying with the dry ash then moved

to landfills. Some coal ash is used for commercial purposes (e.g., cement additive). Leachate infiltration into ground waters immediately below and adjacent to ash disposal sites is not well studied. Data are lacking on chemical species present; chemical form governs mobility, availability, and toxicity. Likewise, there are few data available on the contribution of settling pond outfalls to the hazardous element burden of surface waters. Direct input of dissolved and suspended trace elements and radionuclides into these waters can have a direct effect on water quality and aquatic life depending on waste water treatment. An understanding of the problems associated with coal waste leachate and runoff containing hazardous elements is essential when we consider that currently 92% of the ash in coal is trapped by precipitators and disposed of on the plant site. Preliminary estimates of trace element releases from coal combustion to ash disposal sites indicate that 12 trace elements, including As, Cd, Hg, Ni, Pb, and U, are released at rates that are > 10% of natural weathering rates, meaning that coal extraction and use is short-circuiting the geochemical cycle for trace elements.

Coal Combustion — Atmospheric Emissions. Evaluation of the ecological effects of trace elements and radionuclides from coal combustion requires information about the kinds and amounts emitted during the combustion process, their transport and deposition in the environment, and their availability, accumulation, and toxicity in ecosystems. Based on an incomplete data set concerning the items described above, it appears that atmospheric releases of trace and radioactive elements are not likely to have significant, detectable effects on the chemical composition of soil, vegetation, and water in the near term. There are however, certain areas of the country where detectable effects may occur (e.g., areas of sandy soils and low fertility or areas with sizable ambient concentrations of trace contaminants). In these areas, several trace elements bear watching. These include: F, Cd, Ni, Tl, Cu, V, Zn, Co, Mo, W, and Hg in terrestrial ecosystems; and As, Cd, Co, Hg, Cu, Pb, and Sn in aquatic environments. Fluoride may warrant special attention because of its reactivity and high toxicity in terrestrial systems.

In dealing with soil-plant relationships, emphasis should be placed on hazardous elements that enter soil in the highest concentration (e.g., Hg, W, Cd, and V); are soluble and thus more available to plants (e.g., Cu, Hg, and Ni); are mobile in the plant and transported to edible tissues (e.g., Ni, Tl, and W); and are most toxic to plant and/or animals and man (e.g., Cd, Ni, F, Tl, V, U, and Hg). Furthermore, recognition should be given to the potential benefi-

cial effects of Mo, Zn, Cu, and Co in terrestrial systems and to the stimulating effects, particularly in respect to eutrophication, of some of the trace elements in aquatic systems. The major pollutants in stack emissions from coal-fired power plants (SO_2 , NO_2 , and their transformation products) are of importance in terms of their interactions (synergisms/antagonisms) with trace elements and radionuclides as well as in terms of their direct effects.

There is an inadequate data base for determining the health effects, present or potential, of the trace elements from coal combustion or conversion plants. There is, however, highly suggestive evidence that some contaminants [e.g., Ni, Cd, Cr (VI), As (III), and F] may constitute potential health problems from either direct toxicity or carcinogenesis. Mercury, Pb, and Cd should be followed closely because current intake levels are near the tolerable intake limits. Radioactive emissions from coal combustion currently contribute $< 1\%$ to background radiation dose from all natural sources. However, they could become a health consideration if bituminous coals with high U content (> 5 ppm) are utilized. Important synergistic effects between certain coal-derived metals and other inorganic and organic substances in the environment can be anticipated, and these may prove important in health effect assessments. In the domain of food and water intake, particularly as affected by ash settling ponds and landfills, no toxicological assessment of trace elements or radionuclides is feasible at this time. However, this should be regarded as a potentially significant health problem area which justifies monitoring of these sites.

National Energy Plan Implications

Implementation of the NEP will result in a doubling of coal extraction and use by 1985 and a tripling by 2000. Industrial boilers currently using gas and oil will switch to coal, and electric utilities will add considerably to their generating capacity through coal combustion. Gasification may become a significant coal consumer before 2000. The NEP calls for application of the Best Available Control Technology (BACT) to new boilers. It is assumed that this application will result in a 1% release of ash from combustion to the atmosphere. Assuming U.S. coals average 5% ash, BACT application in 1985 will result in 0.6 million tons of fly ash released to the atmosphere and 59.4 million tons of solid wastes requiring disposal in settling ponds or landfills. Conversion of industrial boilers to coal will serve to disperse sources of particulates to air and will require additional ash disposal areas. Regional air and water quality may change under this dispersed concept.

Trace element and radionuclide effects on health and the environment must be looked at from the point of view of the impact of the NEP on the coal fuel cycle and the relative contribution of hazardous elements from coal contrasted with other sources of regional and local environmental burdens.

Coal Extraction, Cleaning, and Storage. The NEP will have a direct impact on coal extraction, cleaning, and storage. Doubling and tripling coal production in the next 25 years will result in increases in acid mine drainage. The amount of the increase will depend upon enforcement of current regulations and those promulgated under the Surface Mining and Reclamation Act. With BACT being applied, western coals are less attractive in the east because of high transportation cost and low BTU content even though they are low sulfur coals. Eastern coal (high sulfur) will be used in plants equipped with SO_2 scrubbers. This leads to a considerable increase in eastern coal mining with attendant acid mine drainage problems. Hazardous elements in mine drainage may reach ground and surface waters with subsequent ingestion by man and other animals. Western coal production will also increase with attendant alkaline mine drainage problems. Coal cleaning, typically restricted to the east and central regions, will increase with leachate and runoff containing hazardous elements moving into ground water. Storage piles will be more widespread with more opportunities for runoff to reach surface waters and perhaps ground waters. Additional mining and cleaning of coal will lead to increased spoils and cleaning wastes. Coal fines from these wastes along with dusts from coal storage areas will serve as fugitive sources of particulates containing hazardous elements to the atmosphere. Depending on local environmental conditions, these particulates may constitute a health hazard. From the point of view of trace elements and radionuclides, the greatest impact of increased coal mining, cleaning, and storage is the additional burden of these elements to air, soil, and water in environments that are already stressed by ambient levels of these and other pollutants. The degree of synergisms occurring among these contaminants is not well known. Potential hazards from elements released in mining and cleaning will be restricted to particular regions, whereas potential hazards from coal storage may exist nationwide.

Coal Combustion — Solid Waste. Application of BACT coupled with a proposed tripling of coal utilization by 2000 will result annually in some 95 million tons of ash requiring disposal. Scrubber sludges for SO_2 control will add to this solid waste disposal problem. Unless new engineering designs are developed for settling ponds and landfills, direct runoff

to surface waters and leachate intrusion into ground water will certainly occur on a larger scale than at present. Trace elements and radionuclides entering surface waters will add to existing burdens and result in degradation of water quality and potential toxic effects on aquatic species. Contamination of drinking water supplies presents a real human hazard for elements such as Cd and Hg which are already near tolerable intake limits, and causes an economic burden in the form of advanced water treatment plants. Although present studies indicate minimal ground water contamination from coal-ash landfills because of attenuation in soils, the national impact of an additional 60 million tons of ash by 2000 will add significantly to the trace element and radionuclide burden in soils and in some cases exceed their buffering capacities, which will lead to accelerated ground water contamination. Further, this additional coal-ash waste will be much more widely distributed across the country as a result of industrial boilers switching to coal added to the new coal-fired boilers put into service. Mobilization of elements through coal combustion already exceeds 10% of natural weathering for several trace toxic elements and can only be expected to increase with increased coal use.

Coal Combustion — Atmospheric Emissions. Particulate emissions from coal combustion and conversion by 2000 are estimated to reach one million tons annually. These emissions will be predominantly in the respirable range and will contribute both trace element and radionuclide insults to plants and animals. Volatile forms of hazardous elements will accompany stack gas emissions. It is difficult to assess the direct health and environmental effects of coal-combustion-derived hazardous elements. Their accelerated release from increased coal use will add, perhaps significantly, to the ambient atmospheric loading from all other sources. Synergistic actions with coal-derived and other organic and inorganic chemicals in the atmosphere will become more important in determining organism response to increased ambient levels. Thus, a major determinant in potential coal-derived hazardous element effects will be the ambient air quality of the region (i.e., industrial vs. rural) receiving the additional burden. The general public health of the U.S. population will be a factor in determining hazardous element effects from the point of view of irritants, co-factors, and physical synergists.

It is unlikely that atmospheric emissions of hazardous elements will have a measurable effect on concentrations in soil, vegetation, and water. In local situations, however, certain trace elements (F) and radionuclides (Rn) may reach levels causing concern because of both increasing coal use and

switching to coals containing higher concentrations of these elements or their parents. Because of the ubiquitous nature of Cd and Hg (and perhaps Pb) and the fact that their daily intake already approaches tolerable levels, these elements may become real health hazards from coal utilization.

Recommendations

The ability to assess the health and environmental impacts of trace elements and radionuclides derived from current and future coal utilization depends on a basic understanding of (a) the chemistry and physics of elements in coal and ash in the natural environment (mining), in settling ponds and landfills (solid wastes), and in fly ash (atmospheric emissions); (b) the physical and biological transport through air, soil, water, and organisms; (c) the interactions among emissions and ambient pollutants, water, and other natural environmental chemicals; and (d) the ecological and human health effects of coal-derived emissions both singly and in the presence of other environmental stresses. Once this information is available, it will be possible to determine reasonable trace and radioactive element release rates as functions of both environmental tolerance and costs associated with effluent controls. Until this information is on hand, certain activities should be pursued.

(1) Characterization of concentrations and physicochemical states of specific trace elements and radionuclides in both atmospheric emissions and aqueous effluents from coal combustion and conversion should be performed. These monitoring activities should be carried out even though hazardous elements are not considered criteria pollutants and their release rates are not regulated. Special attention should be given to characterization of elements, including As, Cd, Cu, Hg, Ni, Pb, and Zn, in leachates from ash disposal systems, to the oxidation states and chemical forms of Ni, As, and Cr, to the nature and occurrence of organometallic compounds, and to the levels of Cd, Be, and fluorides in terrestrial environments within 40 km of coal-fired power plants.

(2) An assessment of the contribution of trace and radioactive elements from the coal fuel cycle relative to all other sources should be made to put coal-derived hazardous elements in proper perspective.

(3) Rapid, reliable methods should be developed to ascertain the movement of water and solutes in the vicinity of coal ash disposal sites.

(4) Watershed-scale mass flow budgets for trace elements from coal mining and processing operations are needed and should be based on both measurement and model simulations.

(5) Models should be developed that accurately track and predict atmospheric transport and diffusion of coal-derived emissions over rugged terrain, during very stable conditions, and over long distances. Special emphasis should be applied to dry deposition on natural surfaces.

(6) Information about chemical and physical behavior of specific hazardous elements in soils and water is needed. Data requirements include rates of solubilization and transformation, phase distributions, chemical form, and availability. The rate and extent of solubilization on a regional basis is also needed.

(7) The role of the coal-derived hazardous elements As, Cd, Cr, Cu, Hg, Ni, and Pb in drinking water should be evaluated in terms of toxicological and carcinogenic potential.

(8) Compliance testing of environmental control technologies for atmospheric emissions should be vigorously pursued with emphasis on improving removal efficiencies for particulates in the respirable size range.

(9) Methods of removing hazardous elements, including As, Cd, Cr, Cu, Hg, Pb, and Zn, from waste streams (i.e., acid mine drainage, coal pile runoff, settling pond outfalls) need to be developed to reduce the environmental contribution from coal utilization.

I wish to thank members of the ORNL Environmental Resource Center who provided invaluable information service during the development of this paper. I also wish to thank the following reviewers whose comments and criticisms were incorporated into this paper: C. W. Gehrs, D. E. Reichle, C. R. Richmond, W. D. Shults, the National Coal Association, and the American Mining Congress.

REFERENCES

1. Comar, C. L., and Nelson, N. Health effects of fossil-fuel combustion products: report of a Workshop. *Environ. Health Perspect.* 12: 149 (1975).
2. Berry, W. L., and Wallace, A. Trace elements in the environment — their role and potential toxicity as related to fossil fuels. A preliminary study. UCLA 12-946, University of California at Los Angeles, 1974.
3. Theis, T. L. The potential trace metal contamination of water resources through the disposal of fly ash. Paper presented at 2nd National Conference on Complete Water Reuse (AIChE/EPA), Chicago, Illinois, May 1975.
4. McBride, J. P., Moore, R. E., Witherspoon, J. P., and Blanco, R. E. Radiological impact of airborne effluents of coal-fired and nuclear power plants. *Science* 202: 1045 (1978).
5. Van Hook, R. I., and Shults, W. D. Eds. Effects of trace contaminants from coal combustion. ERDA 77-64, National Technical Information Service, Springfield, Va., 1977, 79 pp.
6. Dvorak, A. J., Brown, C. D., Dettman, E. H., Hinchman, R. A., Jastrow, J. D., Kornegay, F. C., La France, C. R., Lewis, B. G., Lundy, R. T., Olsen, R. D., Parker, J. I., Pentecost, E. D., Saquinsin, J. L., and Vinikour, W. S. The environmental effects of using coal for generating electricity. NUREG-0252. U.S. Nuclear Regulatory Commission, Washington, D.C., 1977, 221 pp.
7. Swanson, V. E., Medlin, J. H., Hatch, J. R., Coleman, S. L., Wood, G. H., Woodruff, S. D., and Hildebrand, R. T. Collection, analysis, and evaluation of coal samples in 1975. U.S. Geological Survey Open-file Report 76-468, U.S. Department of the Interior Geological Survey, 1976.
8. Abernethy, R. F., Peterson, M. J., and Gibson, F. H. Spectrochemical Analyses of Coal Ash for Trace Elements. U.S. Bureau of Mines RI7281, 1969.
9. Magee, E. M., Hall, H. J., and Varga, G. M., Jr. Potential Pollutants in Fossil Fuels. U.S. Environmental Protection Agency. PB-225039, National Technical Information Service, Springfield, Va., 1973.
10. Goldstein, N. P., Sun, K. H., and Gonzales, J. L. Radioactivity in fly ash from a coal-burning power plant. *Trans. Am. Nucl. Soc.* 14: 66 (1971).
11. Hill, R. D. Mine drainage treatment — state of art and research needs. U.S. Department of the Interior, Cincinnati, Ohio, 1968.
12. Appalachian Regional Commission. Acid Mine Drainage in Appalachia. Washington, D.C., 1969.
13. McWhorter, D. B., Skogerboe, R. K., and Skogerboe, G. W. Water quality control in mine spoils, Upper Colorado River Basin. U.S. Environmental Protection Agency, Washington, D.C., 1975.
14. Department of the Army. Final Environmental Impact Statement, Sherburne County Generating Plant, Sherburne County, Minnesota. U.S. Engineer District, St. Paul, Minn., 1974.
15. Theis, T. L., Westrick, J. D., Hsu, C. L., and Marley, J. J. Field investigations of trace metals in ground water from fly ash disposal. *J. Water Pollut. Control Fed.* 50: 2457 (1978).
16. Klein, D. H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W., Lyon, W. S., Ogle, J. S., Talmi, Y., Van Hook, R. I., and Bolton, N. Pathways of thirty-seven trace elements through a coal-fired power plant. *Environ. Sci. Technol.* 9: 973 (1975).
17. Natusch, D. F. S., and Wallace, J. R. Urban aerosol toxicity: The influence of particle size. *Science* 186: 695 (1974).
18. Jones, H. C. personal communication.
19. Energy Research and Development Administration. Annual Environmental Analysis Report, Volume I, Technical Summary, Washington, D.C., 1977.
20. Crawford, T. V., Connor, J. J., Cushing, C. E., Dixon, K. R., Dutt, G. R., Gatz, D. E., Goldstein, R. A., Groth, E., Hosker, R. P., Nielsen, D. R., Patterson, M. R., Slinn, W. G. N., and Sharma, V. Environmental Transport. pp. 21-38. In: Effects of Trace Contaminants from Coal Combustion, R. I. Van Hook and W. D. Shults, Eds., ERDA 77-64, National Technical Information Service, Springfield, Va., 1977, 79 pp.
21. Slade, D. H., Ed. Meteorology and Atomic Energy — 1968. TID-24190. National Technical Information Service, Springfield, Va., 1968, 445 pp.
22. ASTM Task Force. Recommended Guide for the Prediction of the Dispersion of Airborne Effluents, 2nd ed., American Society of Mechanical Engineers, New York, 1973.
23. Gatz, D. F. Scavenging ratio measurements in METROMEX. pp. 71-81. In: Precipitation Scavenging (ERDA Symposium Series 41), R. G. Semonin and R. W. Beadle (coords.), CONF-741003, National Technical Information Service, Springfield, Va., 1976, 856 pp.
24. Slinn, W. G. N. Some approximations for the wet and dry removal of particles and gases from the atmosphere. *Water Air Soil Pollut.*, in press.
25. Junge, C. E. Atmospheric Chemistry and Radioactivity. Academic Press, New York, 1963, 382 pp.

26. Engelmann, R. J. The calculation of precipitation scavenging. pp. 208-221. IN: *Meteorology and Atomic Energy* — 1968, D. H. Slade, ed., TID-24190, National Technical Information Service, Springfield, Va., 1968, 445 pp.
27. Chamberlain, A. C. Pollution in plant canopies. In: *Heat and Mass Transfer in The Biosphere, Part I*, D. A. deVries, and N. A. Afgan, Eds., Wiley, New York, 1975, pp. 561-582.
28. Slinn, W. G. N. Dry deposition and resuspension of aerosol particles — a new look at some old problems. In: *Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants* (ERDA Symposium Series 38), CONF-740921, National Technical Information Service, Springfield, Va., 1976, pp. 1-40.
29. Rosinski, J., Langer, G., Nagamoto, C. T., and Bogard, J. S. Generation of secondary particles from single land particles upon impact. In: *Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants* (ERDA Symposium Series 38), CONF-740921, National Technical Information Service, Springfield, Va., 1976, pp. 638-647.
30. Gillette, D. A. Production of fine dust by wind erosion of soil: effect of wind and soil texture. In: *Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants* (ERDA Symposium Series 38), CONF-740921, National Technical Information Service, Springfield, Va., 1976, pp. 591-624.
31. Fields, D. E. CHNSED, Simulation of sediment and trace contaminant transport with sediment/contaminant interaction. ORNL/NSF/EATC-19, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1976, 204 pp.
32. Elwood, J. W. Ecological aspects of tritium behavior in the environment. *Nucl. Saf.* 12: 326 (1971).
33. Underwood, E. J. *Trace Elements in Human and Animal Nutrition*. Academic Press, New York, 1971.
34. Lagerwerff, J. V. Lead, mercury, and cadmium as environmental contaminants. In: *Micronutrients in Agriculture*, J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay, Eds., Soil Science Society of America, Madison, Wisc., 1972, pp. 593-636.
35. D'Itri, F. M. *The Environmental Mercury Problem*. CRC Press, Cleveland, Ohio, 1972.
36. Thompson, S. E., Burton, C. A., Quinn, D. J., and Ng, Y. C. Concentration factors of chemical elements in edible aquatic organisms. UCRL-50564, Lawrence Livermore Laboratory, Livermore, Calif., 1972.
37. Van Hook, R. I. Cadmium, lead, and zinc distributions between earthworms and soils: potentials for biological accumulation. *Bull. Environ. Contam. Toxicol.* 12: 509 (1974).
38. National Academy of Sciences. *Principles for Evaluating Chemicals in the Environment*. Washington, D.C., 1975.
39. Fimreite, N., Holsworth, W. N., Keith, J. A., Pearce, P. A., and Gruchy, I. M. Mercury in fish and fish-eating birds near sites of industrial contamination in Canada. *Can. Field Nat.* 85: 211 (1971).
40. Van Hook, R. I. Transport and transformation pathways of hazardous chemicals from solid waste disposal, *Environ. Health Perspect.* in press.
41. Alexander, M. Biochemical ecology of microorganisms. In: *Annual Review of Microbiology*, C. E. Clifton, S. Raffel, and M. P. Starr, Eds., Annual Reviews Inc., Palo Alto, Calif., 1971, pp. 361-392.
42. Ehrlich, H. L. Biochemistry of the minor elements in soil. In: *Soil Biochemistry*, A. D. McLaren and J. Skugans, Eds., Vol. 2, Marcel Dekker, New York, 1971.
43. Ridley, W. P., Dizikes, L. J., and Wood, J. M. Biomethylation of toxic elements in the environment. *Science* 197: 329 (1977).
44. Wood, J. M. Biological cycles for toxic elements in the environment. *Science* 183: 1049 (1974).
45. Ridley, W. P., Dizikes, L., Cheh, A., and Wood, J. M. Recent studies on biomethylation and demethylation of toxic elements. *Environ. Health Perspect.* 19: 43 (1977).
46. Friberg, L., et al. *Cadmium in the Environment*. CRC Press, Cleveland, Ohio, 1974.
47. Magos, L. Problems of simultaneous exposure to two or more foreign compounds. IN: *Proceedings, IAEA Symposium on Comparative Studies of Food and Environmental Contamination*. IAEA-SM/175, International Atomic Energy Agency, Vienna, 1974, pp. 505-514.
48. Vaughan, B. E., Abel, K. H., Cataldo, D. A., Hales, J. M., Home, C. E., Rancitelli, L. A., Routson, R. C., Wildung, R. E., and Wolf, E. G. Review of potential impact on health and environmental quality from metals entering the environment as a result of coal utilization. Battelle Energy Program Report, Battelle Memorial Institute, Richland, Wash., 1975, 75 pp.
49. Jones, H. C., Andren, A. W., Buffington, J. D., Berry, W. L., Eaton, J. C., Franklin, R. E., Heck, W. W., Horton, J. H., Lewis, R. A., O'Toole, J. J., Shriner, D. S., and Wildung, R. E. Ecological effects. pp. 39-56. In: *Effects of Trace Contaminants from Coal Combustion*, R. I. Van Hook and W. D. Shults, Eds., ERDA 77-64, National Technical Information Service, Springfield, Va., 79 pp.
50. Martin, J. E., Harward, E. D., and Oakley, D. T. Comparison of radioactivity from fossil-fuel and nuclear power plants. *Environmental Effects of Producing Electric Power — Part I*. Appendix 14. Committee Print, Joint Committee on Atomic Energy 91st Congress of the U.S., 1st Session, Washington, D.C., 1969.
51. Kendeigh, S. C. *Ecology with Special Reference To Animals and Man*. Prentice-Hall, New York, 1974, 474 pp.
52. Herricks, E. E., and Cairns, J., Jr. Rehabilitation of streams receiving acid mine drainage. *Bull. 66*. Virginia Water Resources Center, Blacksburg, Va., 1975, 284 pp.
53. Martin, J. F. Quality and effluents from coal refuse piles. In: *Proceedings, First Symposium on Mine and Preparation Plant Refuse Disposal*. National Coal Association, Washington, D.C., 1974, pp. 26-37.
54. Federal Power Commission. Steam-electric plant air and water control data for the year ending December 31, 1972. Federal Power Commission Report FPC-S-246. Washington, D.C., 1975.
55. Holland, W. F., Wilde, K. A., Parr, J. L., Lowell, P. S., and Pohler, R. F. Environmental effects of trace elements from ponded ash and scrubber sludge. *Electric Power Research Institute Report No. 202*, Palo Alto, Calif., 1975.
56. Cushman, R. M., Hildebrand, S. G., Strand, R. H., and Anderson, R. M. The toxicity of 35 trace elements in coal to freshwater biota: a data base with automated retrieval capabilities. ORNL/TM-5793, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1977, 45 pp.
57. Brackett, C. F. Production and utilization of ash in the United States. U.S. Bureau of Mines Information Circular 8488, U.S. Department of the Interior, Washington, D.C., 1972.
58. Klein, D. H., Andren, A. W., and Bolton, N. E. Trace element discharges from coal combustion for power production. *Water Air Soil Pollut.* 5: 71 (1975).
59. Block, C., and Dams, R. Study of fly ash emission during combustion of coal. *Environ. Sci. Technol.* 10: 1011 (1976).
60. Cannon, H. L., and Swanson, V. E. Contributions of major and minor elements to soils and vegetation by the coal-fired Four Corners Power Plant, San Juan Pueblo, New Mexico. U.S. Geological Survey Open File Report No. 75-170, U.S. Geological Survey, Denver, Colo. 1976, 36 pp.
61. Horton, J. H., Dorsett, R. S., and Cooper, R. E. Trace elements in the terrestrial environment of a coal-fired power

- erhouse. DP-1475. Savannah River Laboratory, Aiken, S.C., 1977.
62. Bolton, N. E., Lyon, W. S., Van Hook, R. I., Andren, A. W., Fulkerson, W., Carter, J. A., and Emery, J. F. Trace element measurements at the coal-fired Allen Steam Plant — Progress Report, June 1971 — January 1973. ORNL/NSF/EP-43, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1973, 83 pp.
 63. Klein, D. H., and Russell, P. Heavy metals: fallout around a power plant. *Environ. Sci. Technol.* 7: 357 (1973).
 64. Schwarz, K. Recent dietary trace element research, exemplified by tin, fluorine, and silicon. *Fed. Proc.* 33: 1748 (1974).
 65. House of Representatives, Committee on Science and Technology. The costs and effects of chronic exposure to low-level pollutants in the environment. Document 49. 94th Congress of the United States, Washington, D.C., 1975, 1457 pp.
 66. McCuen, D. C. On establishment of air quality criteria, with reference to the effects of atmospheric fluorine on vegetation. Air Quality Monograph 69-3. American Petroleum Institute, New York, 1968.
 67. Tyler, G. Effects of heavy metal pollution on decomposition and mineralization rates in forest soils. In: International Conference on Heavy Metals in the Environment, Toronto, Canada, Oct. 1975, Vol. II, Part 1, p. 217.
 68. Tyler, G. Heavy metals pollute nature, may reduce productivity. *Ambio* 1: 52 (1972).
 69. Morrow, P. E., Bingham, E., Borg, D. C., Coffin, D. L., Fowler, B. A., French, J., Headley, L. C., Hemphill, D. D., Hopps, H. C., Mahaffey, K. R., Magos, D. L., Nettesheim, P., Norris, W. P., Pfitzer, E. A., and Witschi, H. R. Health effects. In: Effects of Trace Contaminants from Coal Combustion, R. I. Van Hook and W. D. Shults, Eds., ERDA 77-64. National Technical Information Service, Springfield, Va., 1977, pp. 61-76.
 70. Council on Environmental Quality (CEQ). Report of the Interagency Working Group on Health and Environmental Effects of Energy Use. Washington, D.C., 1974.
 71. Hamilton, L. D., and Morris, S. C. Health effects of fossil-fuel power plants. In: Proceedings, 8th Midyear Topical Symposium on Population Exposures. Health Physics Society, Knoxville, Tennessee, October 1974, pp. 305-317.
 72. Morgan, W. R. C. Coal workers pneumoconiosis. *Va. Med. Monogr.* 96: 712 (1969).
 73. Hull, A. P. Radiation in perspective: some comparisons of the environmental risks from nuclear and fossil-fueled power plants. *Nucl. Saf.* 12: 85 (1971).
 74. Turner, W. D., Kaye, S. V., and Rohwer, P. S. EXREM and INREM computer codes for estimating radiation doses to populations from construction of a sea-level canal with nuclear explosives. K-1752. Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tenn., 1968.
 75. Booth, R. S., and Kaye, S. V. A preliminary systems analysis model of radioactivity transfer to man from deposition in a terrestrial environment. ORNL/TM-3135. Oak Ridge National Laboratory, Oak Ridge, Tenn., 1971, 21 pp.
 76. National Council on Radiation Protection and Measurements (NCRP). Natural Background Radiation In The United States. Report No. 45, Pergamon Press, New York, 1975.
 77. Waldbott, G. L. Health Effects of Environmental Pollutants. C. V. Mosby, St. Louis, Mo., 1973, 316 pp.
 78. Pinkerton, C., Creason, J. P., Hammer, D. I., and Colucci, A. V. Multimedia indices of environmental trace-metal exposure in humans. In: Trace Element Metabolism in Animals, University Park Press, Baltimore, Md., 1974.
 79. Mahaffey, K. R., Corneliussen, P. E., Jelinek, C. F., and Fiorino, J. A. Heavy metal exposure from foods. *Environ. Health Perspectives* 12: 63 (1975).